Exposure assessment to heavy metals in general population in a polluted area through biological monitoring

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Summary
In polluted areas, a major issue is the correct assessment of the exposure of general population to industrial pollutants. The objectives were: to evaluate the exposure to heavy metals emitted from industrial area of Taranto; to correlate biological monitoring data with environmental data, in order to clarify the impact of industrial pollution in terms of internal dose. A cross sectional study has been designed to measure levels of urinary arsenic, lead, cadmium, chromium, manganese in 300 inhabitants of Taranto, Statte and Laterza. Adult subjects have been selected by a two-stage random stratified sampling. Results are based on 272 subjects (131 men and 141 women). The observed concentrations of metals in the whole study population are overall high. The median values for lead (7.4 µg/l) and chromium (0.4 µg/l) are higher than the 95th percentile of the range of reference values. For manganese and arsenic the 95th percentile of concentration in the whole study population is higher than the 95th percentile of the range of reference values. Concentrations of mercury in the whole study population are comparable to reference.

Key words: heavy metals, environmental exposure, biological monitoring, cross sectional study

Introduction
Taranto is a town on the Ionic sea in the South of Italy, where many sources of air pollutants are located nearby the urban area. Industrial area includes a large integrated cycle steel factory, a refinery and a cement factory. In the province of Taranto an area at “high risk of environmental crisis”, that includes the municipalities of Taranto, Statte, Massafra, Montemesola, Crispiano, has been identified by Italian Ministry of Environment. A major issue in polluted areas is the correct assessment of the exposure of general population to industrial pollutants.

The objectives were: to evaluate the exposure to heavy metals emitted from the industrial area of Taranto and to compare the exposure between subjects living in the “polluted area” and in a “non-polluted area”; to correlate biological monitoring data with environmental data, in order to clarify the impact of industrial pollution in terms of internal dose.

Materials and Methods
A cross sectional study has been designed to measure levels of urinary arsenic (iAs+MMA+DMA), lead (Pb), mercury (Hg), chromium (Cr), manganese (Mn) in 300 subjects resident, aged 19-65 years old, in Taranto, in Statte (a small town close to the industrial area) and Laterza, a rural town considered the “blank” site, from January 2010 to April 2012. Moreover, municipality of Taranto was disaggregated into three areas: the working class neighbourhood “Paolo VI”, the closest to industrial area
neighborhood “Tamburi - Old Town” and “New Town”, that includes the rest of the city. Adult subjects have been selected by a two-stage random sampling, stratified by age and gender and 30 subjects have been enrolled as volunteers. Each subject in the study has been asked to sign the informed consent form and has been administered by qualified health personnel a structured standardized questionnaire to collect personal data in order to control for potential confounders such as smoking habits, water consumption, presence of fireplace at home and use of pesticides or paints. The analysis of urinary samples has been performed by the Industrial Toxicology Laboratory of the Occupational Medicine Section “B. Ramazzini” of the University of Bari using Atomic Absorption Spectrophotometer. For the determination of As, Cr, Cu, Pb, Mn and As, the cold vapor hydride procedure with generation of arsine was employed; for Hg determination, the graphite furnace method.

Comparisons among groups have been performed by non-parametric methods (Wilcoxon rank sum test and Kruskall Wallis test). A p-value ≤0.05 was considered significant. Statistical analysis was conducted using SAS (v. 9.0) and STATA (v. 11).

Results and Discussion

Results are based on 272 subjects, including 30 volunteers (131 men and 141 women) (mean age±SD= 43.1±13.0).

The table 2 shows descriptive statistics of metals concentrations in urine and the reference range (5th-95th percentile in non occupational exposed population) provided by Italian Society of Reference Values (SIVR). It is notable that for Pb, Cr, Mn and As, the 95th percentile in study population was comparable to SIVR reference range.

**Arsenic:** median value is higher in men (4.1 µg/l) than in women (3.8 µg/l); in the 15-19 years age-group (7.4 µg/l); in smokers (4.2 µg/l) than in non-smokers (3.8 µg/l); between consumers of mineral water (4.2 µg/l) than aqueduct water (3.6 µg/l); between who ate fish the day before the interview (4.75 µg/l vs 3.8 µg/l) or shellfish (crustacean or mollusc) 24-48 hours before the interview (9.8 µg/l and 8.3 µg/l respectively).

The median concentrations disaggregated by city are: 8.8 µg/l in Statte, 3.8 µg/l in Taranto and 2.75 µg/l in Laterza. Among the neighbourhoods of Taranto the highest median concentration was observed in Tamburi-Old Town (4.6 µg/l vs 3.8 µg/l in New Town and 2.7 µg/l in Paolo VI).

Differences in urinary concentrations are statistically significant by city and among Taranto neighbourhoods, and in subjects which consumed shellfish (crustacean) in the 24-48 hours prior to the collection of urinary samples.

**Chromium:** median urinary levels of chromium are similar in both sexes, by age-groups, between smokers and no-smokers and between consumers of waters.

The median concentrations by city are: 0.5 µg/l in Statte, 0.3 µg/l in Taranto and 0.35 µg/l in Laterza with a statistically significant difference.

Among the neighbourhoods of Taranto the highest median chromium concentration was observed in Paolo VI (0.4 µg/l vs 0.3µg/l in the others) but differences are not statistically significant.

**Manganese:** median values are higher in women than in men (1.4 vs. 1.2 µg/l), in the 25-29 years age-group (2.0 µg/l), between smokers and no-smokers (1.7 vs. 1.2 µg/l).

The median concentrations by city are: 0.5 µg/l in Statte, 1.6 µg/l in Taranto and 2.4 µg/l in Laterza with a statistically significant difference.

Among the neighbourhoods of Taranto the highest median concentration was in Paolo VI (2.2 µg/l vs 1.6µg/l in New Town and 0.75 in Tamburi-Old Town µg/l) with a statistically significant differences.

**Mercury:** median urinary levels of mercury are higher in men than in women (1.0 µg/l vs 0.8 µg/l), in the 40-44 years age-group (1.3 µg/l), in smokers (1.1 vs. 0.8 µg/l). The median concentrations by city are: 1.8 µg/l in Statte, 0.7 µg/l in Taranto and 0.8 µg/l in Laterza and intergroup difference is statistically significant. Median concentrations are significantly different among the neighbourhoods of the Taranto (0.9 µg/l in Tamburi-Old Town vs 0.8 µg/l in Paolo VI.
and 0.6 µg/l in New Town).

Differences in median urinary concentration are statistically significant by age and in subjects who had consumed shellfish (crustacean) 48-72 hours prior to the collection of urinary samples.

**Lead:** median concentrations are similar in both sexes (7.3 µg/l in men and 7.5 µg/l in women), between consumers of mineral or acqueduct water (7.5 µg/l vs. 7.4µg/l). Median values are higher in the 55-59 years age-group (6.2 µg/l) than in remaining age-groups.

The concentrations by city are: 12.1 µg/l in Statte, 7.3 µg/l in Taranto and 4.2 µg/l in Laterza and this difference is statistically significant.

Among the neighbourhoods of Taranto the highest median concentration was observed in New Town (7.4 µg/l vs. 7.3µg/l in Tamburi-Old Town and 6.9 µg/l in Paolo VI).

Differences in median urinary concentrations are statistically significant in subjects which ate fish 72 hours (8 µg/l vs 7.2 µg/l) prior to the collection of urinary samples.

<table>
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<th></th>
<th>As µg/l</th>
<th>Cr µg/l</th>
<th>Mn µg/l</th>
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<th>Pb µg/l</th>
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<td>2.7</td>
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</table>

Table 2: Descriptive statistics of metals concentrations measured in a sample of subject.

**Conclusion**

Results from biological monitoring can allow to address the issue of preventing harmful effects of environmental factors and they can be related with environmental emission data, like those provided by EMEP (European Monitoring and Evaluation Programme).

For the whole province of Taranto the value of emissions of Pb into the atmosphere in 2009 was 38 tons, one the highest in Europe, and the emissions of Hg in the same year was 510 Kg. There are no available data concerning emissions of the other metals.

The observed concentrations of metals in the whole study population are overall high. The median values for Pb (7.4 µg/l) and Cr (0.4 µg/l) are higher than the 95° percentile of the range of reference values provided by SIVR (3.5 and 0.32 respectively). For both the metals the highest median concentration has been found in subjects from Statte, the town closest to the industrial area.

For Mn and As the 95° percentile of concentration in the whole study population is higher than the 95° percentile of the range of SIVR reference values. Median concentration of As is higher in Statte than in Taranto and Laterza, while the highest concentration of Mn has been found in Laterza and these results deserve further investigations.

Concentrations of Hg in the whole study population are comparable to reference values and they are higher in Statte than in Taranto and Laterza.

The overall biomonitoring data support the existence of an environmental impairment by heavy metals in the area of Taranto and mostly in the municipality of Statte. This condition can be related to the presence of industrial plants, and in particular of a large integrated steel cycle factory in the area, even if the concentration of Mn, that could be considered a marker of steel factory emissions has been found to be higher in Laterza (the “blank” site) than in Statte and Taranto. Occupational exposures could have determined these findings and further investigations are necessary.

We observed statistically significant differences in urinary excretion of arsenic (iAs+MMA+DMA) in subjects which consumed shellfish in the 24-48 hours prior to the collection of urinary samples. These results confirms the suggestions of other authoritative studies to recommended arsenic exposed workers to abstain from eating sea food in the 1-2 days prior to the collection of urinary samples to determine the levels of arsenic.

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References

- IARC. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Chromium and chromium compounds. 49 Lyon; IARC; 1990
- Società Italiana per i valori di riferimento. 2° lista dei valori di riferimento per elementi metallici, composti organici e loro metaboliti. 2° Ed rivista e corretta. Pavia; SIVR; 2005